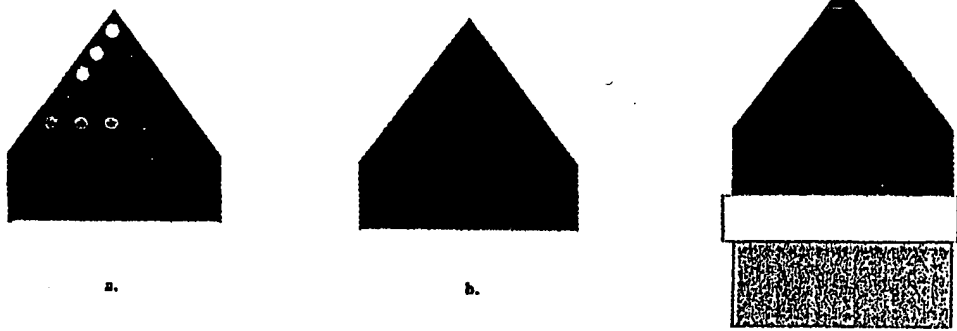


PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : G01N	A2	(11) International Publication Number: WO 00/04362 (43) International Publication Date: 27 January 2000 (27.01.00)
<p>(21) International Application Number: PCT/US99/12520</p> <p>(22) International Filing Date: 4 June 1999 (04.06.99)</p> <p>(30) Priority Data: 60/088,294 5 June 1998 (05.06.98) US</p> <p>(71) Applicant: THE PENN STATE RESEARCH FOUNDATION [US/US]; 304 Old Main, University Park, PA 16802 (US).</p> <p>(72) Inventors: MALLOUK, Thomas, E.; 515 West Prospect Avenue, State College, PA 16801 (US). SMOTKIN, Eugene; 10 West 33rd Street, Chicago, IL 60616 (US). REDDINGTON, Erik; 112 Pleasant Street, Woburn, MA 01801 (US). SAPIENZA, Anthony; 1207 Clearbrook Road, West Chester, PA 19380-3941 (US).</p> <p>(74) Agents: NELSON, Gregory, A. et al.; Quarles & Brady LLP, 222 Lakeview Avenue, 14th floor, P.O. Box 3188, West Palm Beach, FL 33402-3188 (US).</p>		<p>(81) Designated States: CA, DE, JP.</p> <p>Published <i>Without international search report and to be republished upon receipt of that report.</i></p>
<p>(54) Title: METHOD OF SCREENING COMPOSITIONS FOR ELECTROCATALYTIC ACTIVITY</p> <div data-bbox="318 1171 1269 1499"></div> <p>(57) Abstract</p> <p>Methods for identifying compositions useful for catalyzing electrochemical reactions are described. The methods involve simultaneously screening a large number of compositions for electrocatalytic activity using a single voltage source.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

METHOD OF SCREENING COMPOSITIONS .
FOR ELECTROCATALYTIC ACTIVITY

Field of the Invention

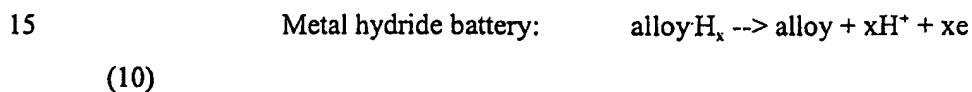
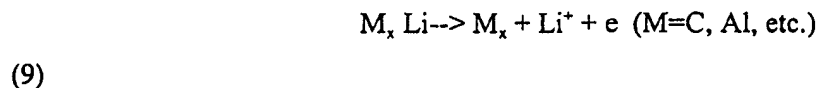
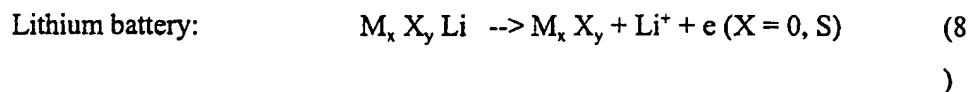
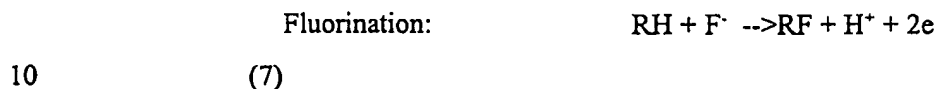
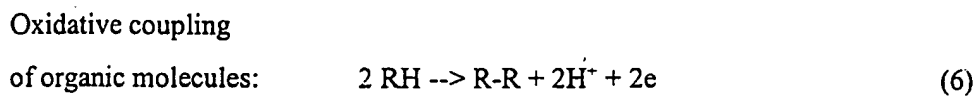
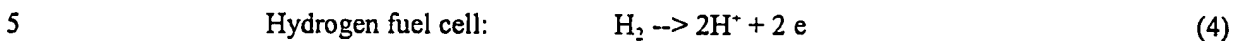
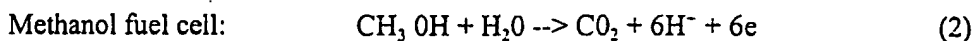
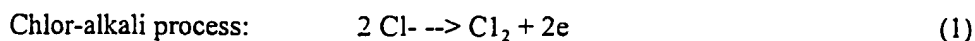
5 The invention relates to methods of screening compositions for particular characteristics. More particularly, this invention relates to an optically-based, highly parallel method of screening a large number of different elemental compositions for the ability to catalyze chemical reactions such as the electrochemical reactions that occur in batteries, fuel cells and the like.

Background of the Invention

10 Electrochemical reactions form the basis of many important commercial applications. Most notably, batteries and fuel cells utilize electrochemical reactions to convert the dormant energy stored in chemical reactants into electricity. Additionally, several large-scale synthetic processes involve electrochemical reactions. Examples of these include the
15 electrolysis of salts or solutions to produce elemental forms of active metals (aluminum, lithium, sodium, magnesium, and others), the chlor-alkali process (in which brine is electrolyzed to make chlorine and caustic soda), the fluorination of organic molecules (Simons process), and the conversion of acrylonitrile to adiponitrile. Other technologies are being developed that utilize electrochemical reactions. These include new electrosynthetic
20 processes (e.g., for producing organic molecules) and new energy-producing devices (e.g., new fuel cells), and devices and methods for corrosion prevention (corrosion being the result of an electrochemical process).

 A distinguishing feature of electrochemical reactions, as opposed to thermal reactions, is that the former involves two half cell reactions that occur in different spatial regions.
25 These two regions (i.e., the anode and cathode) contact the same solution, or contact two different gas or liquid compartments connected by a tonically conducting pathway, such as a membrane or a salt bridge. The anode and cathode may be separated by macroscopic distances (as in electrosynthetic reactions), by a thin electrolyte layer or membrane (as in secondary batteries and fuel cells), or by millimeter or sub-millimeter distances (as in some

corrosion reactions). Half-cell reactions create or consume ions. Examples are given below:



In each of these reactions, the performance and therefore the profit arising from the commercial application are limited by the materials used. The first five examples require electrocatalysts that perform the desired reaction at minimal overpotential to reduce energy costs or maximize the efficiency of energy conversion. The electrocatalyst must also perform the desired reaction specifically, and not perform undesirable side reactions that reduce the

20

yield of products or generate unwanted byproducts. In the last two examples, better electrode materials, with higher energy storage capacity and better charge/discharge characteristics (current density, polarization, cycle life) are sought. Although the need is great, prior to the invention described herein, few, if any, predictive models are available to guide one to the precise composition of a new catalyst. That is, while mechanistic insight gives rise to some predictive guidelines about catalyst compositions, they are rough guidelines. To find really good catalysts, which often lie in narrow composition regions, a rapid empirical screening method is needed.

Conventionally, compositions are individually tested for electrocatalytic activity by incorporating the composition to be tested in an electrochemical reaction device and then making a direct measurement of an electrochemical parameter (e.g., current as a function of potential). If an array of electrodes is generated on a single substrate, each individual electrode is individually contacted in order to directly test each possible electrocatalyst. To simultaneously screen such an array, the same number of meters as compositions to be tested would be required. Thus, practical considerations, limit the conventional technique to screening only small arrays (< 100 compositions), as the technique becomes increasingly unwieldy as the number of compositions per array is increased.

In other fields, a technique known as combinatorial chemistry has been used to identify materials useful for a particular purpose from a multitude of different molecules with unknown characteristics. Combinatorial chemistry is the process of performing several hundred or thousand reactions in parallel to quickly target the chemical substance that has the properties desired. This approach is most useful when little is known about a system, or when models for predicting molecular behavior do not work well. Essentially, it is an

Edisonian approach to optimization of composition that is performed much more rapidly than individual testing of each possible candidate.

The process of combinatorial chemistry was first actually applied in materials discovery. See Hanak, J.S., *J. Mater. Sci.* 5:964, 1970. It was in the field of biochemistry, however, that combinatorial chemistry technology blossomed. The process proved to be a useful tool for screening molecules for binding site selectivity and drug discovery. See, e.g., Fodor et al., *Science* 251:761, 1991; Lam et al., *Nature* 354:82, 1991; Houghten et al., *Nature* 354:84, 1991; Bock et al., *Nature* 355:564, 1992; Cho et al., *Science* 261:1303, 1993; et al., *J. Med. Chem.* 37:2678, 1994; Bunin, et al., *J. Am. Chem. Soc.* 114:10997, 1992; Virgilio et al., *J. Am. Chem. Soc.* 116:11580, 1994; DeWitt et al., *Proc. Natl. Acad. Sci. U.S.A.* 90:6909, 1993; Campbell et al., *J. Am. Chem. Soc.* 117: 5381, 1995; Boyce et al., *Am. Chem. Soc.* 116:7955, 1994; Ohlmeyer, et al., *Proc. Natl. Acad. Sci. U.S.A.* 90:10922, 1993; Bourchardt et al., *J. Am. Chem. Soc.* 116:373, 1994; and Torneiro et al., *J. Am. Chem. Soc.* 117:5887, 1995. It has more recently been used for materials applications in searching for SERS active metals (Baker, et al., *J. Am. Chem. Soc.* 118:8721, 1996), magnetoresistivity (Briceno et al., *Science*, 270:273, 1995), and superconductivity (Xiang et al., *Science*, 268:1738, 1995). A rudimentary application of this method has also recently been applied to screen a small number of ternary metal alloys for electrocatalytic activity. Mallouk, et al., *Fuel Cell Seminar Extended Abstracts*, Orlando, FL, November 1996, pp. 686-689. Some of these methods have uncovered materials that exhibited the desired properties with stoichiometries that could not be predicted by known science. Despite these advances, prior to the invention described herein, a combinatorial chemistry-based method useful for screening large numbers of complex metal alloys was unknown.

Summary of the Invention

A screening method for identifying new materials for use as catalysts (e.g., electrodes) in electrochemical reactions, such as those that occur in fuel cells, batteries, corrosion protection and the like has been discovered. The essence of the invention is that a change in concentration of the ions produced or consumed in the electrode reaction is sensed optically or by similar means. These local concentration changes occur in the solution or membrane contacting the material being screened, and are largest where the local current density is largest. The invention thus involves preparing an array consisting of several compositions of unknown catalytic activity printed onto a electrically conducting substrate. The printed array is used as an electrode in an electrochemical reaction device. A potential is applied to the electrode array. In response, different portions of the array generate different local concentrations of ions. Thus, using a molecular probe which emits a signal in response to changes in local ion concentration, spots on the array where good catalysts are present can be identified. These spots can thereafter be analyzed for their chemical make up. If the array was fabricated according to a predetermined pattern, the make up of the chemicals at each spot can be readily determined by reference to the pattern.

Accordingly, the invention features a method for screening a plurality of compositions for electrocatalytic activity, the method including the steps of: providing a test composition made up of a mixture of at least a first substance and a second substance, depositing a predetermined quantity of the test composition onto a discrete area on a substrate to form a test device, placing the test device into a reaction cell that contains a medium and an ion concentration indicator; applying a potential to the test device in the reaction cell, applying an excitation radiation to the test device in the reaction cell, and measuring an emission radiation

from the discrete area on the substrate in the reaction cell as an indication of the electrocatalytic performance of the test composition.

In the foregoing method, the first substance and second substance can be metal salts, and the mixture can include a metal alloy.

5 In some methods within the invention, the test compositions are deposited on the substrate using an ink jet printer. A substrate useful in the invention is Toray carbon.

The medium in the method can be methanol or a gas such as oxygen or reformat gas. The ion concentration indicator used in the invention can be fluorescent pH indicator, such as a base sensitive pH indicator, e.g., Phloxine B.

The excitation radiation can be ultraviolet light, and the emission radiation can be measured optically.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, the preferred methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

Other features and advantages of the invention will be apparent from the following detailed description, and from the claims.

Brief Description of the Drawings

Figure 1 depicts the preparation Toray carbon substrates for use as arrays in the invention.

Figure 2 depicts the unfolding of a quaternary phase diagram.

5 Figure 3 depicts an array being screened for efficient catalysts in a methanol/water cell containing a fluorescent pH indicator.

Figure 4 is a diagram of a gas diffusion cell useful in the invention.

Figure 5 is a diagram of a two piece combinatorial gas diffusion cell useful in the invention.

10 Figure 6 shows an electrode is a series of quaternary precursor composition maps for Pt-Ru-Mo-Rh-Ir compositions that manifest zones of high activity for reformat gas electro-oxidation, as determined by optical screening. Darker spots indicate regions of higher activity.

15 Figure 7 is a pentanary precursor composition map for Pt-Ru-Mo-Rh-Ir compositions that manifest zones of high activity for reformat gas electro-oxidation, as determined by optical screening. Ir content increase progressively (11, 22, 33, 44, and 55 atomic percent) from left to right. Darker spots indicate regions of higher activity.

Figure 8 shows quaternary and pentanary precursor composition maps for unsupported Mo-Pt-Ru-Rh-Ir compositions that manifest zones of high activity as oxygen electroreduction catalysts, as determined by optical screening. In the pentanary map, Ir content increase progressively (11, 22, 33, 44, and 55 atomic percent) from left to right. Larger or darker spots indicate regions of higher activity.

Figure 9 shows quaternary and pentanary precursor composition maps for carbon-supported Rh-Pt-Ru-Os-Ir compositions that manifest zones of high activity as oxygen electroreduction catalysts, as determined by optical screening. In the pentanary map, Ir content increase progressively (11, 22, 33, 44, and 55 atomic percent) from left to right. Larger or darker spots indicate regions of higher activity.

Detailed Description

The invention relates to a method for simultaneously screening a large number of compositions for electrocatalytic activity using a single voltage source. Rather than directly measuring the current produced from each composition in response to an applied potential, the electrocatalytic activity of several individual compositions is simultaneously measured using an indirect method. In this combinatorial chemistry-based procedure, an array of tens to thousands of compositions (e.g., electrodes) of differing elements is simultaneously prepared, tested, and then ranked for the desired properties.

The method of the invention involves several steps. First, the compositions to be tested for catalytic activity are applied to an electrically conducting substrate to form an array. This array is placed into an electrochemical reaction device. A potential is then applied to

the array to induce any electrocatalytic activity present. As electrochemical reactions produce and consume ions, different portions of the array generate different local concentrations of ions in accordance to how catalytic that portion of the array is. Spots on the array where efficient catalysts have been applied can thus be identified using a molecular probe that emits a signal in response to changes in local ion concentration. The chemical make up of the compositions correlating to these spots can be determined by chemical analysis, or preferably, by referring back to how the compositions were originally applied on the substrate. Using this method, many different kinds of electrochemical reactions can be monitored including, but not limited to, oxidation and reduction of organic molecules, oxidation of hydrogen, reduction of oxygen, reduction of nitric oxides, oxidation or reduction of carbon monoxide, uptake or release of lithium ions, and formation or electrochemical discharge of metal hydrides.

Preparation of Electrode Arrays

The substrate on which the array is based is selected for particular characteristics and thus depends on many variables including the nature of the materials to be applied thereto, the chemical reactions the array is to be subjected to, as well as the environment the array is to be used in. For example, if the array is to be used at high temperatures or extreme pH's, materials that can withstand such environments should be chosen. Several substrates suitable for such applications are available commercially. For the preferred embodiments described herein, Toray carbon paper has proven to be a suitable substrate. In particular this substrate is useful because it is electrically conductive but not catalytic. Additionally, its thin carbon fibers also help hold the compositions to be tested to the substrate. In some applications, the substrate is

rendered hydrophobic (e.g., by coating with Teflon), in order to make it compatible with other devices.

The array is prepared by applying the compositions to be screened onto the substrate. The compositions tested can be any compositions desired that are compatible with the substrate. These compositions can be applied to the substrate by any conventional means. For example, the compositions can be dissolved in a liquid and then pipetted onto the substrate. In particular adaptations of the invention, a series of metal alloys is fabricated and applied onto the substrate for testing.

Referring to Figure 1, arrays for testing electrocatalytic activity are fabricated by applying a series of different metal alloys on a single substrate. Metal alloys can be prepared according to methods known in the art, including for example, electrochemical reduction of metal salt mixtures, arc-melting, annealing metal colloids, vapor phase deposition, and electroplating. For the purposes of testing such alloys for catalytic activity, however, the preferred method for use in the invention is the chemical reduction of metal salts. More specifically, metal alloys are prepared from the corresponding metal salts by mixing the desired salts together in the appropriate molar ratio in an aqueous solution and then adding a chemical reducing agent to form the alloy. See, e.g., McKee, D.W., and Norton, F.J., *Journal of Catalysis*, 3:252, 1964; and McKee, D.W., *Journal of Catalysis*, 14:355, 1969. Suitable chemical reducing agents include borohydride, hydrogen gas, formaldehyde, hydroxylamine, and hydrazine. The alloy particles thus formed can be applied onto the substrate for analysis. In many cases, the atomic ratio of the metals comprising the alloy can be altered by simply varying the quantity of each metal salt added to the mixture.

In a more preferred embodiment, aqueous solutions of individual metal salts or mixed

metal salts are applied to the substrate prior to the reduction step. After the metal salts have been applied on the substrate, the chemical reducing agent (e.g., aqueous sodium borohydride) is added so that the salts are reduced to zero valent metals directly on the substrate.

5 Aqueous metal salt solutions can be applied to the substrate by any convention method capable of delivering small volumes of liquid precisely and accurately. For example, the salt solutions can be applied to the substrate using a microliter syringe or a micropipet. Each different composition to be tested is applied to a discrete area or "spot" on the substrate in order to avoid any cross contamination. In preferred embodiments, the metal salt solutions
10 are printed onto the substrate using an ink jet printer (e.g., an Apple Stylewriter 2500). Use of such printers enables precise quantities of the salt solutions to be delivered onto substrates including Toray carbon paper. Moreover, the pattern and molar ratios of the applied salt solutions can be controlled using commercial drawing software (e.g., by drawing each ink in gray scale). Among other methods, the printer can be calibrated by ultraviolet-visible
15 spectroscopy by printing a highly absorbing organic dye onto the transparencies and then desorbing each spot into a known volume of solution. Thus, in the preferred method, the compositions to be tested are prepared by dispensing precursor inks containing the appropriate metal salts (e.g., H_2PtCl_6 , RuCl_3 , Na_2MoO_4 , RhCl_3 , K_2IrCl_6 and OsCl_3) dissolved in an aqueous solution (e.g., typically 1-2 M in water, or a glycerol/water mixture) onto
20 Toray carbon paper by use of an ink jet printer. The metals are then reduced with a 40 fold molar excess of borohydride. After printing and reduction, the newly formed arrays are rinsed thoroughly with water and dried.

Mapping

It is preferred that the individual spots on the arrays of the invention be applied in an intuitive pattern. That is, the alloys to be tested should be spotted onto the substrate according to a predetermined pattern or "map" based on set parameters such as the molar ratios of metal in alloys to be tested. The advantage of this method is that after measuring a response from an array, the map can be consulted to pinpoint what composition is giving a particular response. This is especially important to avoid confusion when a large number of compositions is to be screened.

An application of this process is shown in Fig. 2, where a map is constructed by unfolding a quaternary phase diagram into two dimensions. The tetrahedral structure in the figure is a three-dimensional guide to the chemical make up of metal alloys containing up to four distinct elemental metals (e.g., M_1 , M_2 , M_3 , and M_4). The spheres at the vertices represent the four distinct metals in their pure elemental form. Spheres in between one or more vertices represent alloys composed of the metals of each vertex in proportion to their linear distance from each vertex.

Arrays can be made according to the pattern of such maps in order to facilitate the analysis of large numbers of test compositions. This mapping approach can be automated using the ink jet printer process described above.

Testing Arrays for Electrocatalytic Activity

Measuring the electrocatalytic activity of compositions can be performed by making a direct measurement of one or more electrochemical parameters. As one example, current can be measured as a function of potential by, for instance, applying a potential to an individual

electrode in an electrochemical reaction device and measuring the current generated. The current produced at a given potential is indicative of the electrocatalytic efficiency of the electrode. Thus, one method of testing the arrays of the invention is to put the array into an electrochemical reaction device, apply a potential to the array, and measure the current produced at each spot in the array using a meter.

In the invention, the preferred method of measuring the electrocatalytic activity of test compositions is a more indirect method. Rather than measuring the current at each spot corresponding to individual test compositions, the pH in the area immediately proximal to each spot is used to estimate that composition's catalytic activity. Reddington et al, *Science*, 280:267 (1998). This pH is modulated in areas on the array having efficiently catalytic compositions because the oxidation and reduction reactions that take place during electrochemical reactions result in the production and consumption of protons, respectively.

Thus, compositions that perform most efficiently produce the greatest pH change at the lowest applied potential. That is, compositions that are more efficient at catalyzing oxidation reactions (i.e., better anode catalysts) cause a more acidic pH in the area immediately surrounding the electrode at a given applied potential than less efficient compositions. Similarly, compositions that are more efficient at catalyzing reduction reactions (i.e., better cathode catalysts) cause a more alkaline pH in the area immediately surrounding the electrode at a given applied potential than less efficient compositions.

Molecular Probes

Molecular probes, also known as chemosensors, are small molecules that produce a measurable signal upon interaction with a specific analyte. See, *Chemosensors of Ion and*

Molecule Recognition. Desvergne, J- P.; Czarnik, A. W., Eds.; NATO ASI Series C: 492; Kluwer: New York, 1997. Myriad probes are available for many different kinds of application. See, e.g., <http://molecularprobes.com>. Molecular probes useful in the invention are those that can produce a measurable signal, such as an emission radiation (e.g., light-based signals such as fluorescence, phosphorescence and luminescence), in response to changing ion concentrations. Among these are fluorescent pH indicators. These probes emit a measurable fluorescent signal that correlates with proton concentration, and therefore are useful for quantifying pH levels. Examples of the pH indicators useful in the invention include among others quinine, Ni^{2+} complexed with 3-pyridin-2-yl-4,5,6-triazolo-1,5-a-pyridine (Ni-PTP), Eosin Y, and Phloxine B. The particular probe used in the methods of the invention should be chosen according to the specific screening method used. For example, for screening compositions for anode catalytic activity, a probe compatible for use in acid environments, e.g., Ni-PTP, may be preferred. Likewise, Phloxine B is suitable for screening for cathode electrocatalysts. Another factor in probe selection is the manner of signal output. Particularly convenient are those probes emitting light-based signals.

Electrochemical Reaction Devices

After rinsing and drying, the array is placed into an electrochemical reaction device for screening (i.e., a screening cell). The cell itself is the apparatus housing the electrochemical reaction for which catalytic compositions are being screened for. Various type of screening cells are known in the art and can be selected according to the catalytic reaction being assessed.

Figure 3a shows an example of a screening cell useful for assessing compositions for

use as anodes. This device is a single-compartment, three-electrode cell housing an electrolytic solution of methanol and water containing a pH-sensitive fluorescent indicator (e.g., acridine, quinine, or Ni-PTP). In a preferred embodiment, the aqueous solution used is 6 M methanol, 0.5 NaClO₄, 30mM Ni(ClO₄)₂, and 100 μM PTP adjusted to pH 3 with HClO₄. The array is electrically contacted and placed in the cell so that it functions as the working electrode. A small overpotential is applied to the array and is made incrementally more anodic. Ultraviolet light (e.g., a handheld UV lamp; 354 nm) is applied to the array as an excitation source for the fluorescent indicator. By modulation of local proton concentration, spots on the array containing efficient catalytic compositions fluoresce in response to the anodic potential. See Figures 3b and 3c. The most efficient catalysts are those that fluoresce at the lowest applied anodic potential.

Other electrochemical reaction devices can be used in the invention. For example, for screening compositions for use as cathode electrocatalysts (e.g., those that catalyze oxygen reduction), a gas diffusion can be used in a manner similar to that described for a methanol-based cell. As shown in Figure 4, a simple immersible gas diffusion cell was machined from 1 cm thick plexiglass and fitted with Teflon tubing connections to gas lines. The area accessible to the electrode is a circle with a diameter of 1 cm. The back side of the electrode was exposed to a flow of the appropriate gas. The open side of the electrode was exposed to solution containing a fluorescent pH indicator (Phloxine B). Two fitted rubber gaskets are used to prevent leaking. The electrode was electrically contacted by a gold foil which is pressed tight between a gasket and the electrode. The cell was tested by comparing various alloy electrocatalysts for oxygen reduction. The gas-diffusion geometry gave acceptable high current density (≥ 10 mA/cm²) at low overpotential. The fluorescent signal from Phloxine B

in the solution contacting the electrode was clearly detectable under these conditions. The cell needed to be in a horizontal orientation to allow maximum throughput of UV excitation light, and to minimize convection-induced streaming of the basic form of the indicator.

As shown in Figure 5, a larger two-piece combinatorial gas diffusion cell was constructed for general purpose use with electrocatalysts for gas-phase reagents. Gases are introduced from the bottom, and the upper component is filled with the electrolyte/fluorescent dye mixture. This cell included a top cover piece and pressure equalizing "snorkel," which allowed it to be immersed in a constant temperature bath. The cell holds a piece of teflonized Toray carbon paper containing a 645-member array representing combinations of five different components.

Examples

Example 1 - Screening Compositions for Catalytic Efficiency

Compositions were prepared and tested according to the method described in Reddington et al., *Science*, 280:1735, 1998. Electrode arrays were prepared in duplicate by printing precursor inks containing salts of the indicated metal (e.g., H_2PtCl_6 , RuCl_3 , Na_2MoO_4 , RhCl_3 , K_2IrCl_6) dissolved in glycerol/water onto a Toray carbon support. Inks were delivered so that each spot in the array contained the same total number of moles of metal prior to the reduction step using an ink jet printer (e.g., an Apple Color Stylewriter 2500 where the pattern for each ink was drawn in grayscale with commercial drawing software). The spots were reduced with a forty-fold molar excess of sodium borohydride, and the arrays were washed repeatedly with deionized water.

The back of the array was made hydrophobic by coating with Teflon[®], and the array

then served as the working electrode in a three-electrode gas diffusion cell. H_2/CO (1 atm/100 ppm) was diffused through the electrode. The other side of the electrode array contacted an electrolyte solution maintained at pH 3 and contained a Ni-PTP (Ni^{+} 3-pyridin-2-yl-<4,5,6>triazolo-<1,5-a>pyridine). After conditioning the array for several minutes in the reformat stream, the potential was gradually increased from -150mV vs. DHE (dynamic hydrogen reference electrode) until visible fluorescence was observed. Bulk catalysts (used in B and C below) were prepared in a similar way, except that the solutions of metal salts were prepared by standard volumetric methods rather than by delivery from an ink-jet printer (e.g., the appropriate quantities of metal salts were dissolved in water to an overall concentration of 2 mM, pH adjusted to 9; a ten-fold excess of 5% wt% sodium borohydride was added one drop at a time; the precipitate washed ten times with water; and dried at 110°C). The supernatant solutions were physically separated from the solid catalysts and analyzed spectrophotometrically for Mo, using the thiocyanate method. Marczenko, Z., *Separation and Spectrophotometric Determination of Elements*, Ellis Horwood: Chichester, 1986. These measurements showed that Mo was quantitatively re-oxidized and dissolved in the washing steps. The solid catalysts were tested unsupported at loadings of 0.4-1.2 mg/cm² in the same fuel gas mixture and on Teflon[®]-coated Toray carbon, in a gas diffusion cell equipped with a DHE and Pt counterelectrode. Current-voltage curves were recorded after an initial conditioning period, during which all catalysts lost some activity, presumably because of CO poisoning.

Precursor compositions (in atomic percent) used to form alloys with catalytic activity precursor compositions were printed onto Toray carbon arrays using the method described above. After washing, little or no Mo remained in the alloys formed. The arrays were

prepared and installed as the working electrode in a three-electrode gas diffusion cell, and then tested for catalytic efficiency according to the above described method. The data obtained is expressed in three-dimensional tetrahedral diagrams shown in Figures 6 and 7 .

The spheres in the diagrams each correspond to particular a particular metal composition

5 tested. Larger or darker spheres are depicted to indicate the compositions that gave a fluorescent signal indicating efficient catalysis. In the quaternary maps, the spheres at each vertex represent compositions 100% (99/99) of the element indicated. Spheres removed one space away from a vertex along a binary edge represent alloys composed 88/99 of the element indicated at the proximal vertex and 11/99 the element indicated at the distal vertex located at
10 the other end of the binary edge. In the same manner, spheres removed two spaces from the a vertex along a binary edge represent alloys having 77/99 of the element indicated at the proximal vertex and 22/99 the element indicated at the distal vertex. This pattern continues in 11/99 increments along the binary edge. Thus spheres located at the vertices represent pure metal and the sphere located in between the vertices along the binary edge represent
15 binary alloys.

The same geometrical pattern continues in the other portions of the tetrahedron. Thus, spheres located on each outer triangular surface of the tetrahedron (except those on the binary edge) represent ternary alloys formed by the three elements indicated at the vertices of the triangle. Similarly, those sphere located in the interior of the tetrahedron represent quaternary
20 alloys. The specific atomic ratios of each element in an alloy represented by a particular sphere can thus be calculated according to its placement in the tetrahedron. For pentanary alloys, the tetrahedral pattern is expanded into four dimensions by plotting a series of tetrahedrons, each of the tetrahedrons representing alloys with varying concentrations of the

fifth element. In these maps, composition atomic percents range from 11-55%, in 11 atomic percent increments.

Example 2: Cathode Catalysts Screening

A. Compositions (in atomic percent) used to form alloys with catalytic activity.

5 The following compositions were prepared and printed onto Toray carbon arrays as described in Example 1 except Os was used instead of Mo. The back of the array was made hydrophobic by coating with Teflon®, and the array then served as the working electrode in a three-electrode gas diffusion cell. Oxygen was diffused through the carbon to simulate the kind of gas diffusion cathode environment found in a typical polymer electrolyte membrane
10 (PEM) cell. The potential of the array was made progressively more negative, starting from a potential at which oxygen is not easily reduced. Phloxine B (active at basic pH's) was used as the fluorescent indicator dye to indicate active catalytic compositions. Compositions that were tested included alloys prepared from the metals listed below wherein the each metal was added at between 0-99 atomic percent in 11 percent increments. The catalytic activity of the
15 compositions is shown in the tetrahedral composition maps shown Figure 8. The elemental compositions of active alloy catalysts generated a visible fluorescent signal as indicated by the larger or darker spots on the tetrahedral composition maps.

Example 3: Screening Compositions for Fuel Cell Cathode (Oxygen reduction)

Catalysts

20 Compositions (in atomic percent) used to form alloys with catalytic activity were prepared in the presence of carbon support material and printed in arrays onto Toray carbon

as described in Example 1. The compositions were tested for catalytic ability using the same method described in Example 2. Compositions that were tested included alloys prepared from various metals added at between 0-99 atomic percent in 11 percent increments. The results are shown in Figure 9. Active catalysts generated a visible fluorescent signal as indicated by the larger or darker spots on the tetrahedral composition maps.

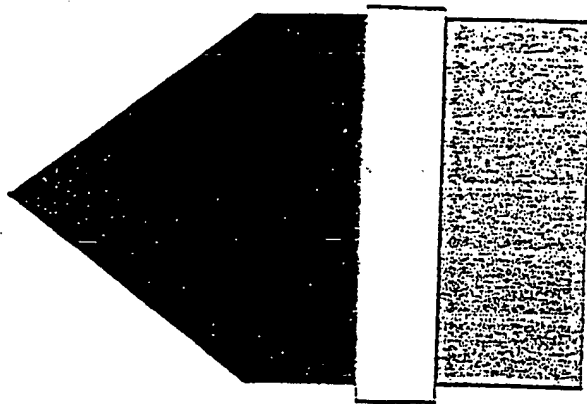
Other Embodiments

It is to be understood that while the invention has been described in conjunction with the detailed description thereof, the foregoing description is intended to illustrate and not limit the scope of the invention, which is defined by the scope of the appended claims. Other aspects, advantages, and modifications are within the scope of the following claims.

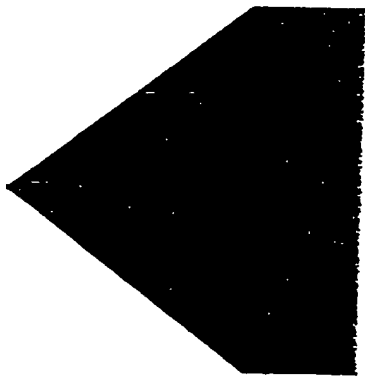
What is claimed is:

- 1 1. A method for screening a plurality of compositions for electrocatalytic
2 activity, said method comprising the steps of:
3 providing a test composition comprising a mixture of at least a first substance and a
4 second substance,
5 depositing a predetermined quantity of said test composition onto a discrete area on a
6 substrate to form a test device;
7 placing said test device into a reaction cell, said reaction cell containing a medium and
8 an ion concentration indicator;
9 applying a potential to said test device in said reaction cell;
10 applying an excitation radiation to said test device in said reaction cell; and
11 measuring an emission radiation from said discrete area on said substrate in said
12 reaction cell as an indication of the electrocatalytic performance of said test composition.
- 1 2. The method of claim 1, wherein said first substance and said second substance
2 are metal salts.
- 1 3. The method of claim 1, wherein said mixture comprises a metal alloy.
- 1 4. The method of claim 1, wherein said test composition is deposited on said
2 substrate using an ink jet printer.

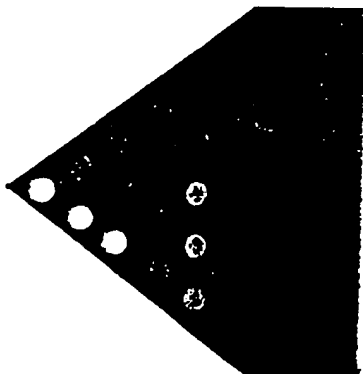
- 1 5. The method of claim 1, wherein said substrate is Toray carbon.
- 1 6. The method of claim 1, wherein said medium is methanol.
- 1 7. The method of claim 1, wherein said medium is a gas.
- 1 8. The method of claim 7, wherein said gas is selected from oxygen and
2 reformat gas.
- 1 9. The method of claim 1, wherein said ion concentration indicator is a
2 fluorescent pH indicator.
- 1 10. The method of claim 9, wherein said fluorescent pH indicator is a base
2 sensitive pH indicator.
- 1 11. The method of claim 10, wherein said base sensitive pH indicator is Phloxine
2 B.
- 1 12. The method of claim 1, wherein said excitation radiation is ultraviolet light.
- 1 13. The method of claim 1, wherein said emission radiation is measured optically.



c

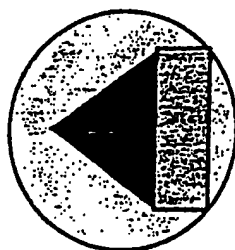
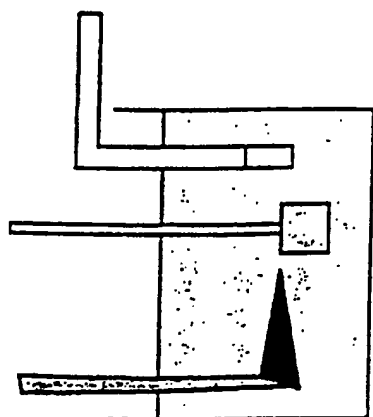


b.

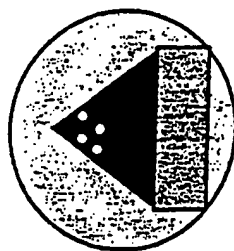


a.

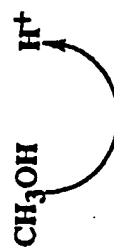
FIGURE 1



INDICATOR



PROTONATED
INDICATOR



a.

b.

c.

FIGURE 3

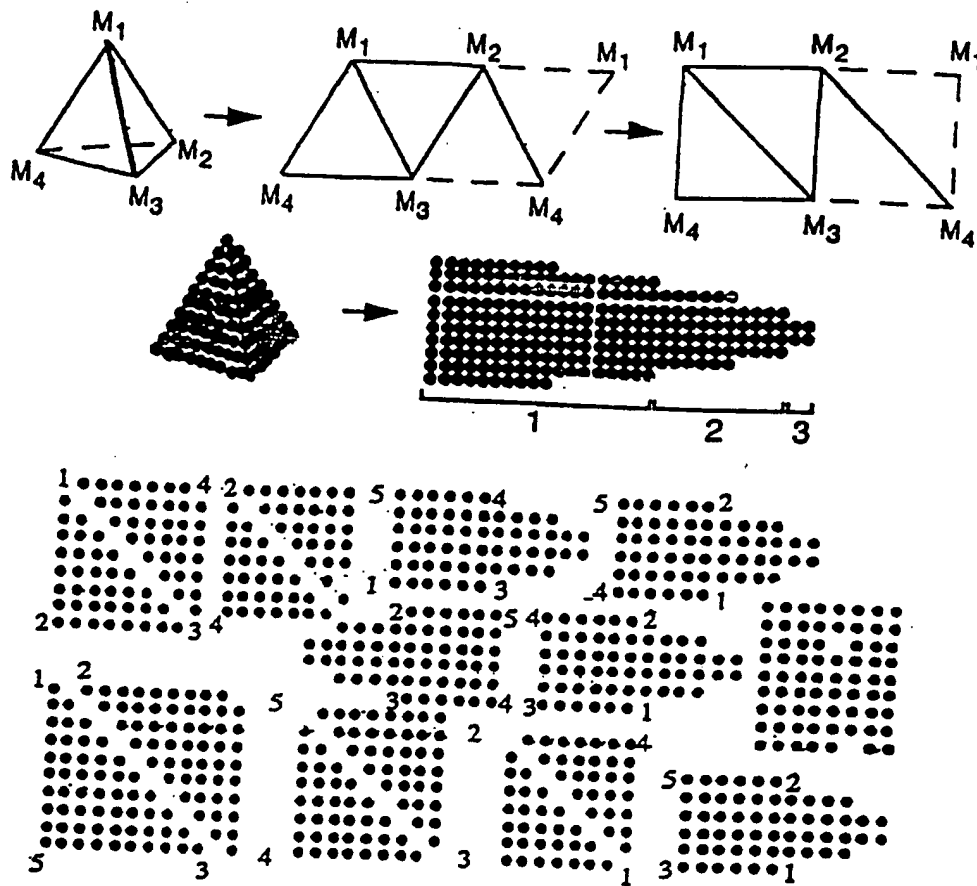


FIGURE 2

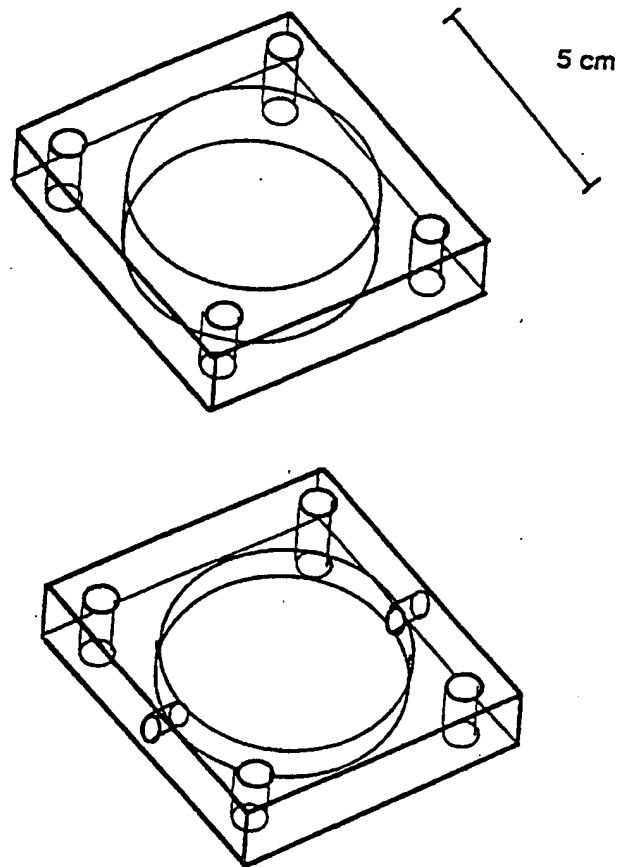


FIGURE 4

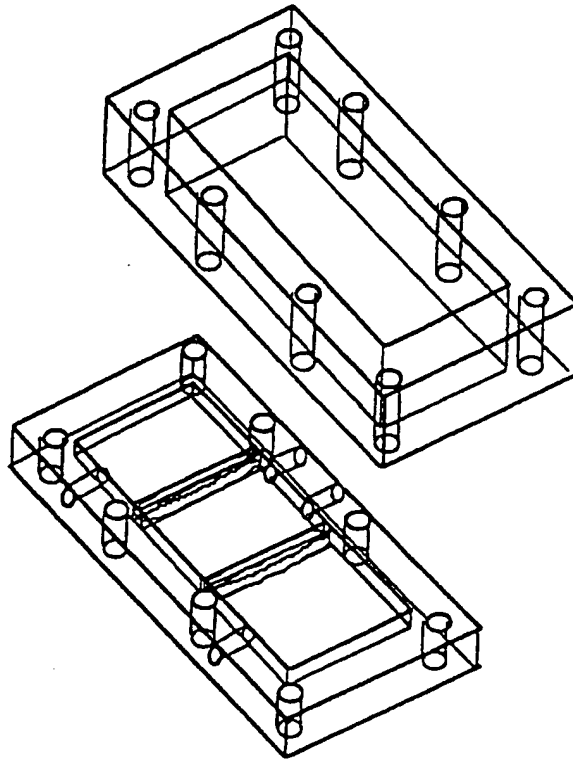


FIGURE 5

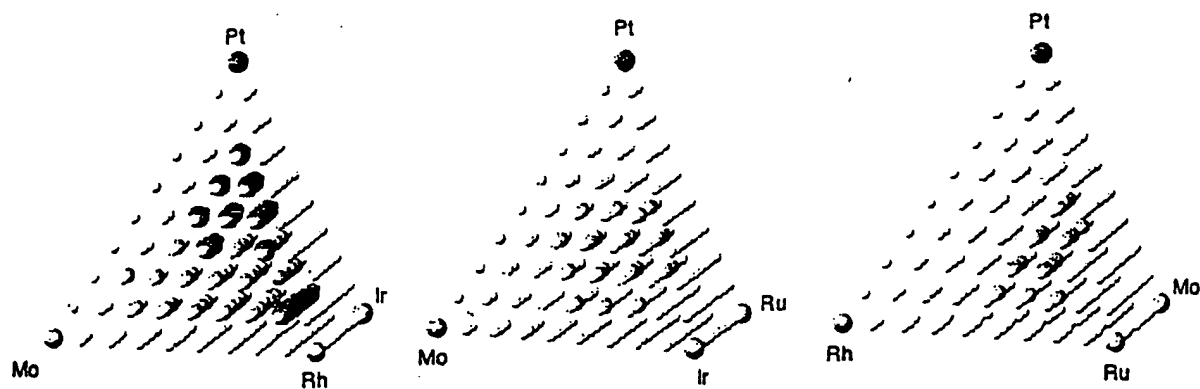


FIGURE 6

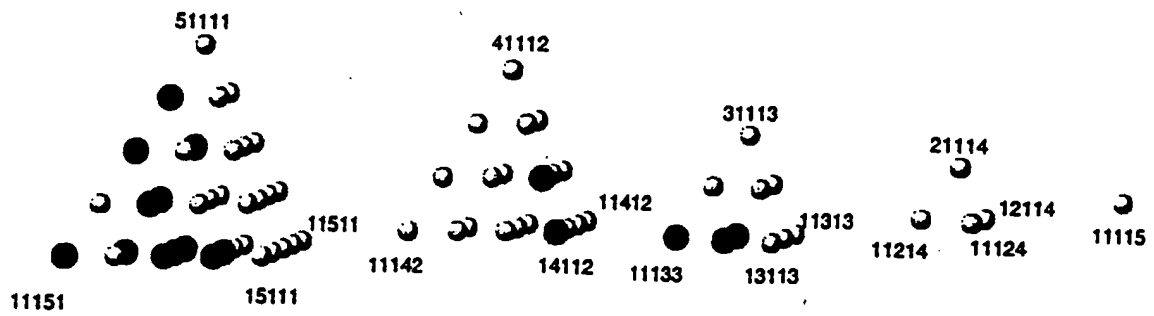


FIGURE 7

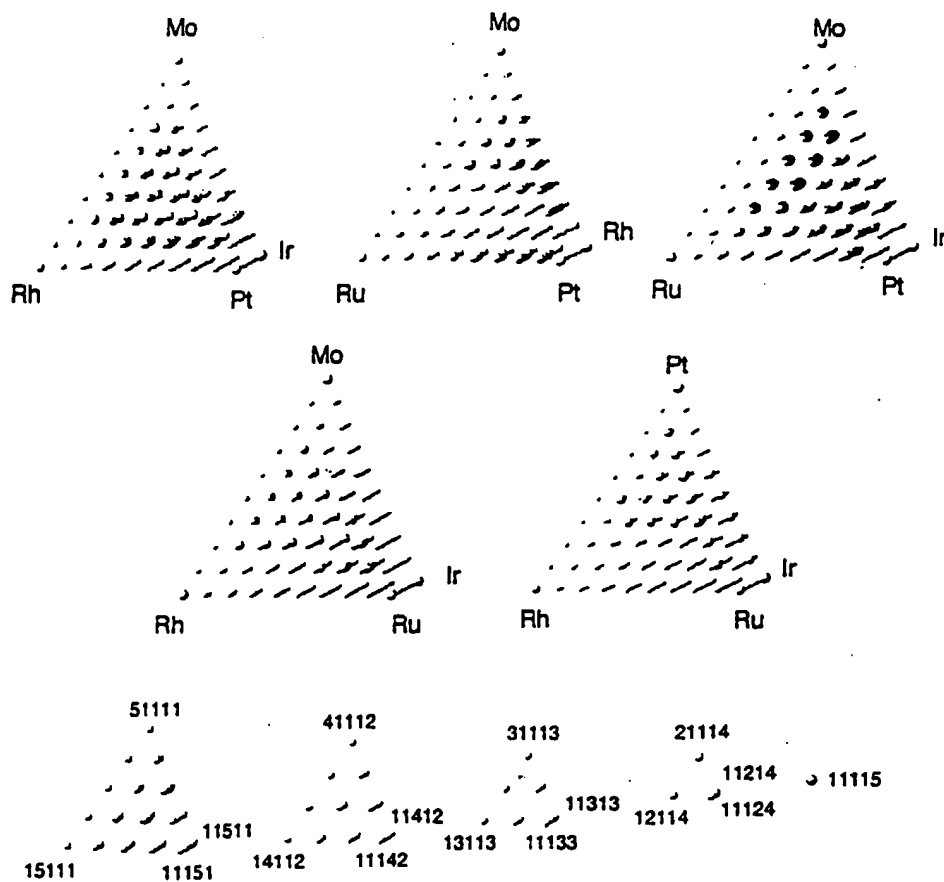


FIGURE 8

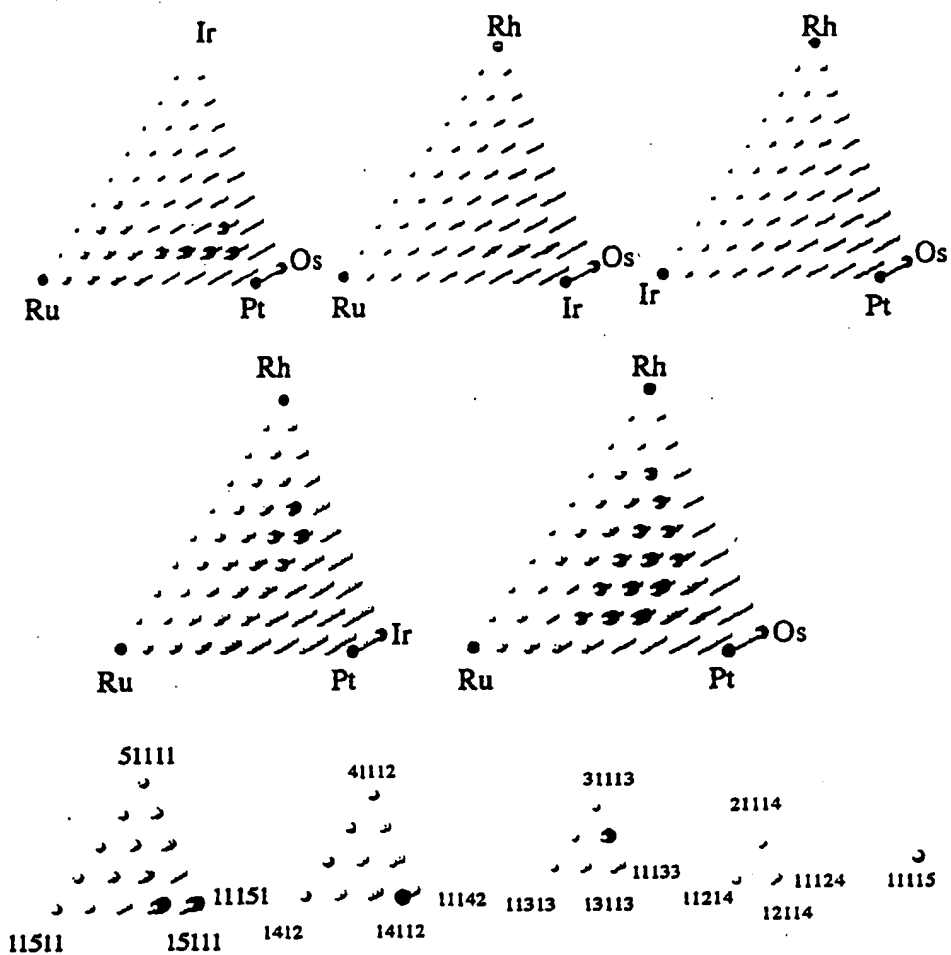


FIGURE 9